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The electron stimulated desorption of Xe from W(110) yields only neutral Xe with cross section $10^{-19} cm^2$. In the presence of preadsorbed oxygen or CO kick off of Xe by electron desorbed oxygen or CO occurs with geometric cross section.

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Electron Impact Desorption of Xe from the Tungsten (110) Plane

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[handwritten annotations: "3×10 to the minus 14th Power Sq. Cm."; "APPX. 10 to the minus 15th power Sq. Cm."; "10 to the minus 17th Power Sq. Cm."; "APPX 10 to the minus 14th Power Sq. Cm."]

ABSTRACT

The electron stimulated desorption of Xe on the clean and on oxygen and CO covered tungsten (110) surfaces has been investigated. Only neutral Xe desorption was observed; a very small initial regime with cross section 10^{-17} cm^2 is followed by a slow decay with cross section 3×10^{-19} cm^2. The Xe yield varies nonlinearly with coverage, suggesting desorption from edges of islands or from sites with less than their full complement of nearest neighbor Xe atoms. Desorption from oxygen or CO covered surfaces results in an apparent desorption cross section identical to that of the underlying adsorbate. This results from a kicking off of Xe by electron desorbed O or CO. The true cross sections for these processes are $\lesssim 10^{-14}$ cm^2 for Xe-O and $\sim 10^{-15}$ cm^2 for Xe-CO. Some speculations about the mechanism, particularly the absence of ions are presented.

Electron impact desorption (or electron stimulated desorption as it is frequently called) is known to lead to the desorption of both neutral and ionic particles in all chemisorption systems studies so far[1]. Studies on physisorbed systems seem to have been confined mostly to CO and O_2 adsorbed on top of chemisorbed layers of CO[2] and O[3] respectively. In the case of these diatomic physisorbates [4], very high initial cross sections for the desorption of neutral CO and O_2 were found, and these species seemed to predominate over all ions, particularly parent ions CO^+ and O^+_2. The explanation advanced for this was that

intramolecular excitation and dissociation of O_2 or CO leads to fragments with kinetic energies in the eV range which can then kick off, in each dissociation event, a considerable number of weakly adsorbed molecules by direct momentum transfer. The purpose of the present work was to investigate the situation for a monatomic, weakly adsorbed species.

EXPERIMENTAL

Experiments were carried out in a stainless steel ultrahigh vacuum system most of whose features have been described in detail previously [5]. For electron impact work a W filament approximately 0.2 to 0.5 cm in front of the crystal was used, as in previous experiments [4], with a UTI quadrupole mass spectrometer ca. 2 cm behind the filament serving as mass analyzer- and detector. In experiments looking for ions, the mass analyzer's electron source was turned off and the crystal kept positive with respect to ground by 45 volts. For measurements of neutrals the mass spectrometer operated normally and crystal and EID filament were kept negative with respect to ground to prevent the penetration of ions into the mass spectrometer. Electron energies of 200 eV were used in all experiments.

In later experiments grids were used to exclude electrons from the mass spectrometer from the crystal region and electrons from the EID filament from the mass spectrometer. Additionally, the cryoshield slit of the effusion source [5] was reduced in length in these series of experiments, so that only the central portion of the crystal, between the potential leads was covered with Xe, to prevent spurious effects arising from EID from the ends of the current or potential leads.

The W crystal was oxygen treated and cleaned by flashing to 2500 K. It was checked for cleanliness by Auger measurements in the usual manner. Xe monolayers were prepared by slight overdosing at 27 K and then heating to 50-55 K. Measurements were carried out with the crystal at 27 K.

RESULTS AND DISCUSSION

It was first attempted to look for the production of various ionic species, i.e. Xe^+, Xe_2^+, Xe^{++}. Within the limits of detection of the apparatus no ion current was found. Thus, for Xe^+, the mass spectrometer signal after amplification was $\leqslant 8 \times 10^{-15}$ amperes for an electron current of 100 microamperes. By comparison, for an 0 covered surface (0/W=0.5) the initial 0^+ signal after the same amplification was 4×10^{-11} amperes for an electron current of 10 microamperes. Consequently, the cross section for Xe^+ production can be estimated to be, assuming comparable angular distributions of 0^+ and Xe^+ ions

$$\sigma_{Xe^+} \leqslant \sigma_{0^+} \left(\frac{8\times10^{-15}}{4\times10^{-11}}\right) \left(\frac{10}{100}\right) \left(\frac{N_{Xe}}{N_0}\right) \left(\frac{T_{0^+}}{T_{Xe^+}}\right) \left(\frac{G_{0^+}}{G_{Xe^+}}\right) \tag{1}$$

where T stands for transmission, G for multiplier gain and N for the coverages in atoms/cm^2. $N_{Xe} = 6\times10^{14}$, $N_0 = 10\times10^{14}$; the initial cross section for 0^+ production has been estimated [4] to be $\sigma_{0^+} = 5\times10^{-22}$ cm^2. $(T_{0^+}/T_{Xe^+}) = 100/23$, $(G_{0^+}/G_{Xe^+}) = (1.2/0.46)$. Consequently, we conclude that $\sigma_{Xe^+} \leqslant 1.5\times10^{-25}$ cm^2. Estimates for other ionic species yield comparable numbers.

Attempts to look for desorption of neutral Xe were successful. Fig. 1 shows a semilogarithmic plot of the mass spectrometer signal vs. time (after subtraction of background) for neutral Xe desorption. There is an initial rapid decay, whose cross section is $\sim10^{-17}$ cm^2, followed by a slower decay whose cross section was found to be 3.2×10^{-19} cm^2 from the slope of the curve. The background to be subtracted consisted of the Xe background gas ionization in the mass spectrometer, and in those experiments where no grids were used, a contribution to gas phase ionization in the mass spectrometer by electrons from the EID filament. This latter contribution was suppressed when the grids were used.

The fast decay portion of the signal is not an artifact. It was found even when the only central portion of the crystal received a Xe deposit. It could not be removed by heating the crystal, even to partial desorption, and in fact persisted to $\theta = 0.25$ when the coverage was reduced by desorption. It increased approximately as $\theta^{1.4}$ when coverage was increased by dosing (Fig. 2). After decay of this initial signal, it could not be restored by heating, but only by redosing with at least .5 monolayers. The total amount of Xe removed by the fast decay process is immeasurably small, either by subsequent thermal desorption or by Auger measurements.

These facts suggest that it results either: (1) from some configurations, which can be created only by dosing but not by diffusive rearrangement of the layer on heating, with a fraction of these configurations surviving thermal desorption, or (2) from kickoff of Xe by EID of an impurity present in small amounts but having a high cross section. The existence of such a kick-off effect for preadsorbed or coadsorbed O or CO will be discussed shortly. Attempts to look for ions other than Xe were therefore made during EID, but proved to be negative. The purity of Xe gas used was also checked with mass spectrometer by closing the poppet valve connecting the main chamber to the pumping section (to reduce spurious liberation of gases from the ion pump during measurements). It was found that the Ar content was $\leqslant 0.1\%$. The impurities in Xe gas were checked by thermal desorption and neither H_2 or N_2 impurities were found. Finally, no impurities such as C, O, N, and Ar were found by Auger Electron spectroscopy for a crystal covered with one monolayer of Xe.

The slow decay exhibits some unusual properties as well. Fig. 3 shows signal intensity vs. coverage, obtained by partial desorption from a full layer. The signal is clearly increasing less than linearly with θ, or looked at another way,

remains at high values as θ decreases. Attempts to obtain a similar curve by
increasing θ by dosing led to such scatter that no firm conclusions could be drawn.
This result may be significant, in indicating that the accidental details of local
adsorption configuration play a role in determining the apparent overall EID yield.
Again, it is difficult to do more than speculate on the reasons for the non-
linearity of yield with coverage. In the thermal desorption of Xe from W(110)
Opila and Gomer [6] found zero order desorption for coverages θ> ~0.3. One pos-
sible explanation of this fact is the existence of islands in such a way that the
total perimeter stays essentially constant; another possible mechanism also in-
vokes the existence of islands. If ESD of Xe occurs primarily from island edges,
the present results could be rationalized by assuming that the curve shown in
Fig. 3 represents a measure of the effective perimeter vs. coverage. At high θ
the perimeter stays (almost) constant, thereby keeping the yield higher. As θ
decreases, the perimeter begins to decrease rapidly, so that the yield drops
rapidly at low θ. It is also possible that desorption occurs from those Xe atoms
having the least number of nearest neighbors, even in the absence of well defined
islands. Again, this quantity can vary very non-linearly with θ. Experiments were
also performed at θ = 2. The Xe signal seemed to be essentially equal to or
slightly lower than that for 1 layer, and the cross section, as determined from
decay curves, was essentially the same as for 1 layer. In the first layer EID
did not seem to be temperature dependent up to T = 35 K.

In view of the nonlinearity of yield with θ, another method for estimating
cross sections was used, namely a direct comparison of the Xe mass spectrometer
signal with that of neutral CO from virgin-CO desorption. By a method entirely
analogous to that embodied by Eq. 1, it was found that $\sigma_{Xe} = 4 \times 10^{-19}$ cm^2, using
the following values: $N_{CO} = 10^{15}$ molecules/cm^2; $\sigma_{CO} = 5 \times 10^{-17}$ cm^2; $T_{Xe}/T_{CO} = .22/1$;

$I_{Xe}/I_{CO} = 2.75/I$, where I is relative ionization efficiency in the mass spectrometer; $G_{Xe}/G_{CO} = 0.45/0.95$; neutral CO signal in the mass spectrometer produced by an electron current of 2.5 microamperes = 3.8×10^{-11} amperes; neutral Xe signal similarly produced by an electron current of 100 microamperes = 2.1×10^{-12} amperes. The σ value so obtained is comparable with that obtained from the decay, particularly since the details of the angular distribution for Xe are not known.

Experiments were also carried out in which Xe was adsorbed on layers of oxygen first adsorbed on the crystal. In these experiments a large neutral Xe signal was seen and decayed somewhat faster than the underlying chemisorbed species. (Figs. 4 and 5). Similar results were found with CO. For this case the mechanism is clearly kick-off of Xe by desorbing neutral and ionic CO or O. The apparently faster decay is due to the combined Xe and oxygen or CO depletion. It was possible to estimate the cross section of the kick-off as follows: If the underlying species is oxygen for instance

$$\left(\frac{\overset{\circ}{n}_{Xe}}{A}\right) = \sigma_{Xe-0} \left(\frac{\overset{\circ}{n}_0}{A}\right) \left(\frac{n_{Xe}}{A}\right) \tag{2}$$

where $\overset{\circ}{n}$ is the rate in atoms/sec, σ_{Xe-0}th kick-off cross section and $n_{Xe}/A = N_{Xe}$ the coverage in atoms/cm^2. $\overset{\circ}{n}_0$ /A the rate at which 0 atoms and ions are produced per cm^2, is given by

$$\overset{\circ}{n}_0/A = \sigma_0 \, (\overset{\circ}{n}_{e-}/A) \, (n_0/A) \tag{3}$$

where σ_0 is the total oxygen desorption cross section and $\overset{\circ}{n}_{e-}/A$ the electron flux. Thus

$$\overset{\circ}{n}_{Xe}/A = \sigma_{Xe-0} \, \sigma_0 \, \left(\frac{\overset{\circ}{n}_{e-}}{A}\right) \, N_0 N_{Xe} \tag{4}$$

and using

$$i_{Xe} = c_{Xe} \; (\overset{o}{n}_{Xe}/A) \qquad\qquad (5)$$

where c_{Xe} converts desorption rate into mass spectrometer signal, we can easily obtain σ_{Xe-0} using as before the relation between neutral CO signal and CO cross section to evaluate c_{Xe}. The results are as follows: For O/W = 0.5 layers heated to 90 K, $\sigma_{Xe-0} = 1.1 \times 10^{-14}$ cm^2, for O/W = 0.5 layers heated to 1100 K, $\sigma_{Xe-0} = 1.2 \times 10^{-15}$ cm^2. For virgin CO layers $\sigma_{Xe-CO} = 1.2 \times 10^{-15}$ cm^2. Thus, the cross sections are essentially geometric. In view of the relative efficiency of momentum transfer and the weak binding of Xe this is reasonable.

It is interesting that heated O layers seem to have a smaller apparent cross section. This suggests that the total amount of oxygen desorbed by EID is much less for layers heated to 1100 K, than for those heated only to 90 K. It is also interesting that the ratio of Xe to 0^+ signal (the latter referring to desorbed O ions) is Xe/0^+ = 2.4 for 90 K oxygen layers and 16 for 1100 K layers. This indicates that after heating to 1100 K the ion/electron yield for 0^+ has decreased even more than the total amount of electron-desorbable oxygen. All of these facts point to reconstruction of the oxygen covered surface after heating to 1100 K.

While the mechanism of apparent Xe ESD in the presence of adsorbates with high true cross sections seems clear, the mechanism of true ESD for Xe is not. The absence of ions suggests one of two possible mechanisms: Initial excitation is to an ionic state, possibly by a non-vertical transition, followed with such high efficiency by neutralization that only neutrals escape. The small overall cross section could then be the result of (a) a small Franck-Condon factor for the initial excitation to a repulsive region of the ionic curve and (b) a high neutralization probability on the part of the curve permitting recapture. On the

other hand, it is possible that initial excitation to an ionic state plays only a very small role, if any, and that most of the observed desorption results from excitation to a repulsive state $Xe^* - M$, or to Xe-Xe repulsion $Xe^* - Xe$. In view of the high mass of Xe and the fact that it is physisorbed not chemisorbed, the first mechanism seems more plausible. Unfortunately, the observed signals are so weak that it is not possible to make cross section vs. excitation energy measurements. It is hoped that experiments on lighter inert gases will permit such measurements.

It is also interesting that the yield of Xe for $\theta = 2$ is not appreciably different from that for $\theta = 1$. In view of the results for Xe adsorbed on oxygen or CO covered surfaces, this suggests one or both of the following: (1) There is a quenching of excited Xe by other Xe atoms, even in the second layer, so that any kick-off is balanced by a reduced desorption probability. (2) The energy of desorbing Xe is so small that even if there is no quenching per se, kick off of a second layer Xe atom results in readsorption of the originally excited first layer atom.

ACKNOWLEDGEMENT

Figure Captions

[1] Semilogarithmic plot of mass spectrometer signal vs. time for neutral Xe in electron impact desorption from a full monolayer at 27 K. Electron current 100 microamperes, electron voltage 200 volts. Also shown are the (extrapolated) fast and slow decay lines.

[2] Plot of intensity of fast decay portion of neutral Xe signal vs. coverage, by dosing. The ordinate consists of the initial total signal in curves like those of Fig. 1, minus the extrapolated slow decay portion.

[3] Initial intensity of slowly decaying portion of neutral Xe signal in EID, as function of coverage. Coverage was reduced, starting from a full monolayer by thermal desorption, and determined from the thermal desorption signal in the mass spectrometer.

[4] 0^+ signal in the EID of Xe adsorbed on an $0/W = 0.5$ layer heated to 90 K before Xe adsorption. The scale of the ordinate corresponds to a mass spectrometer current of 0.19×10^{-10} amperes (after multiplication) per division. Electron current 25 microamperes, electron energy 150 volts. The 0^+ signal is not appreciably affected by the presence by Xe.

[5] Neutral Xe signal in the EID process described in Fig. 4. All conditions and scales as in Fig. 4. Note the faster decay of the Xe signal.

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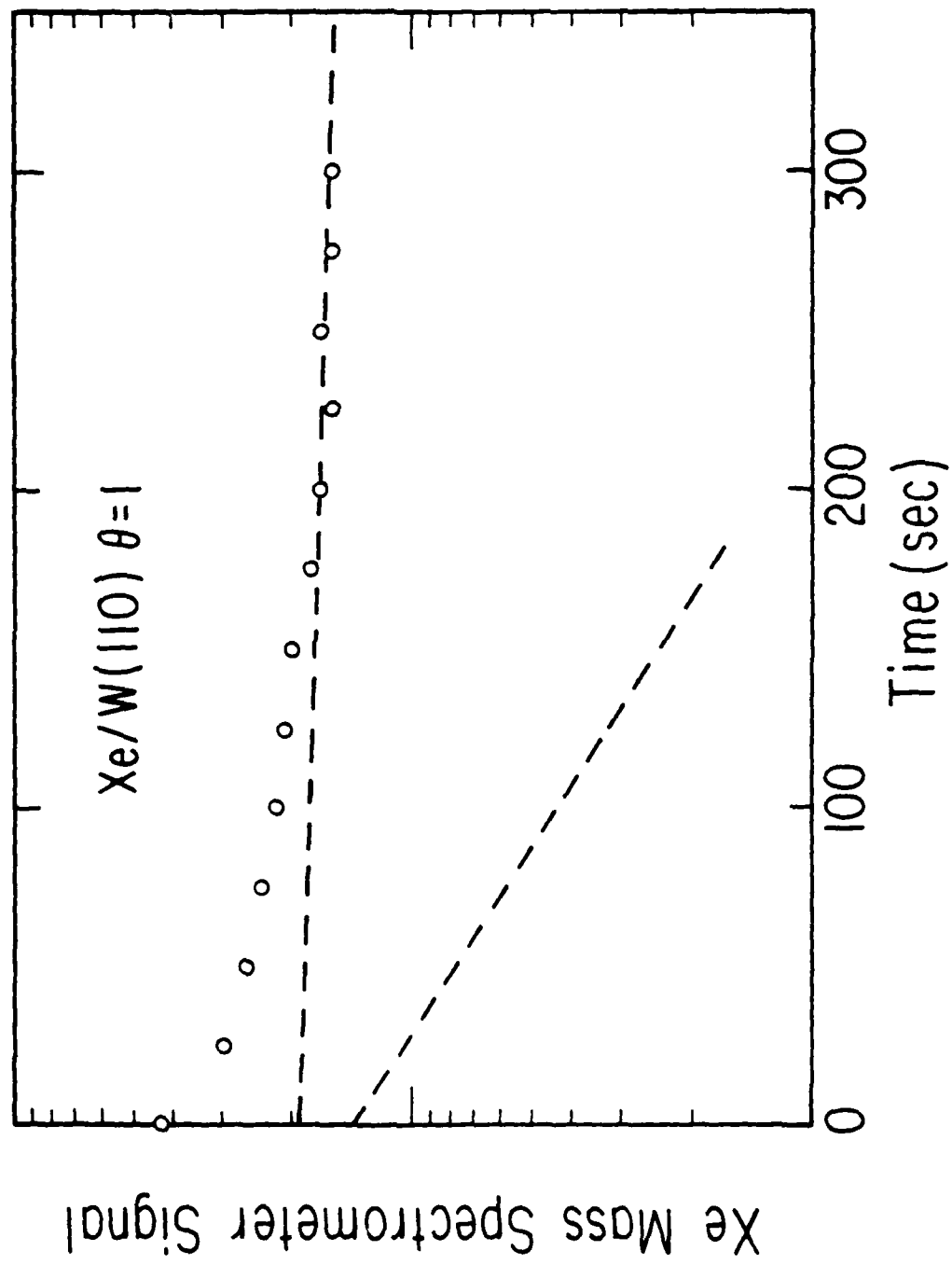* On leave of absence from Fudan University, Shanghai, China.

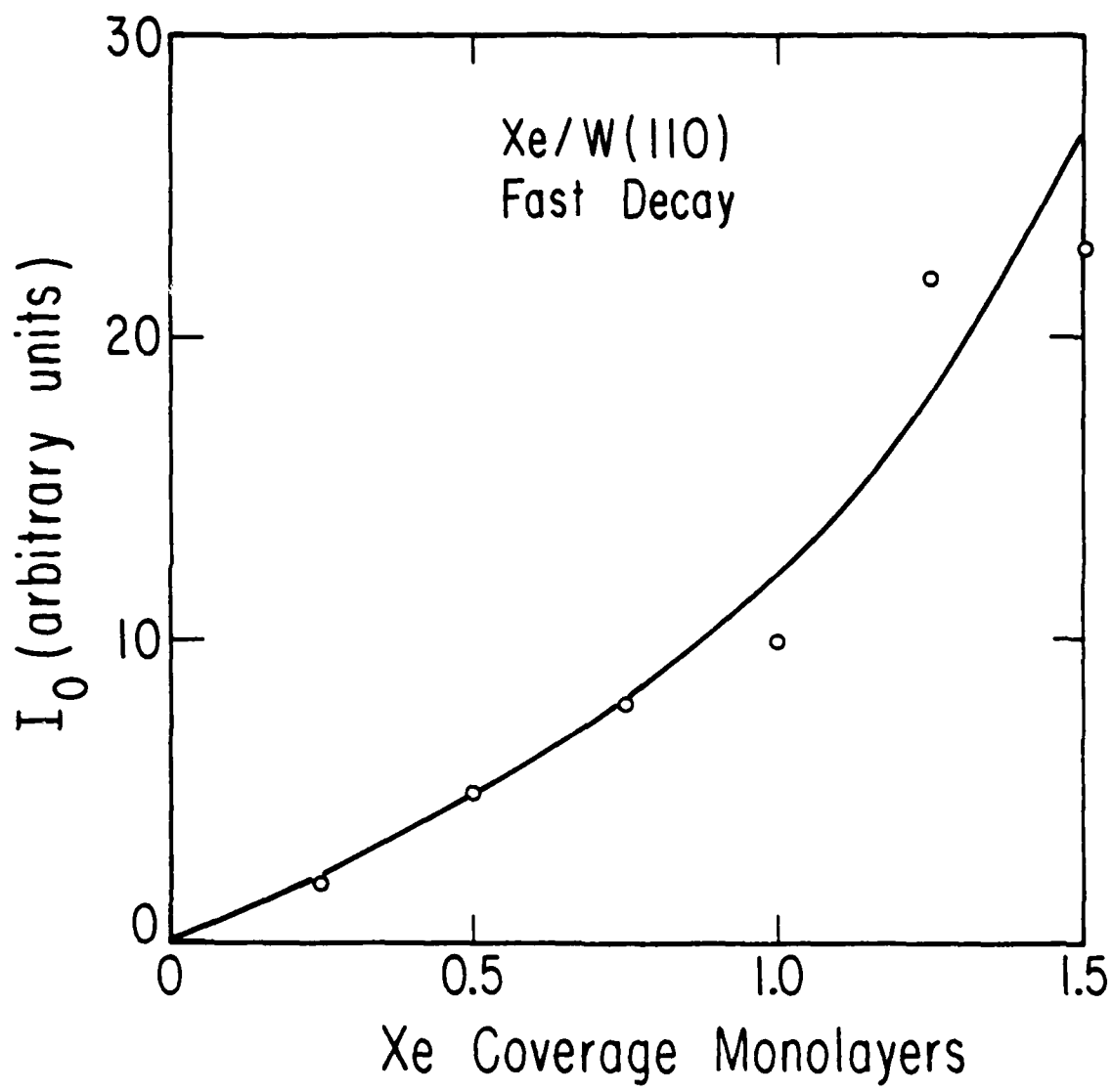Xe/W(110) θ=1
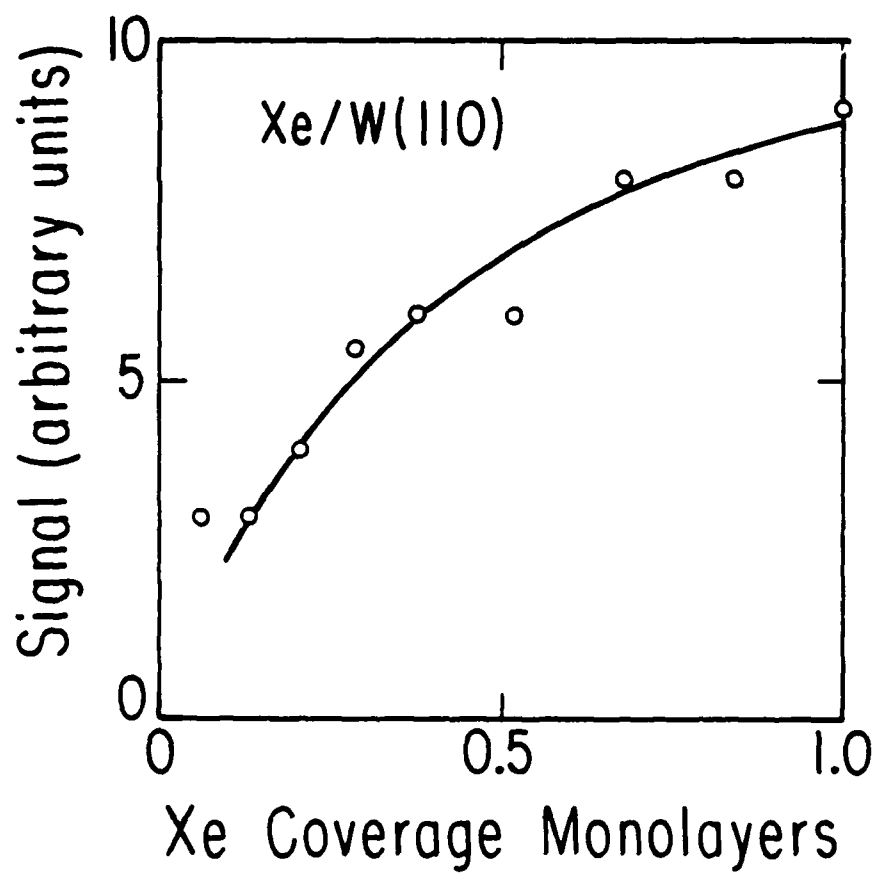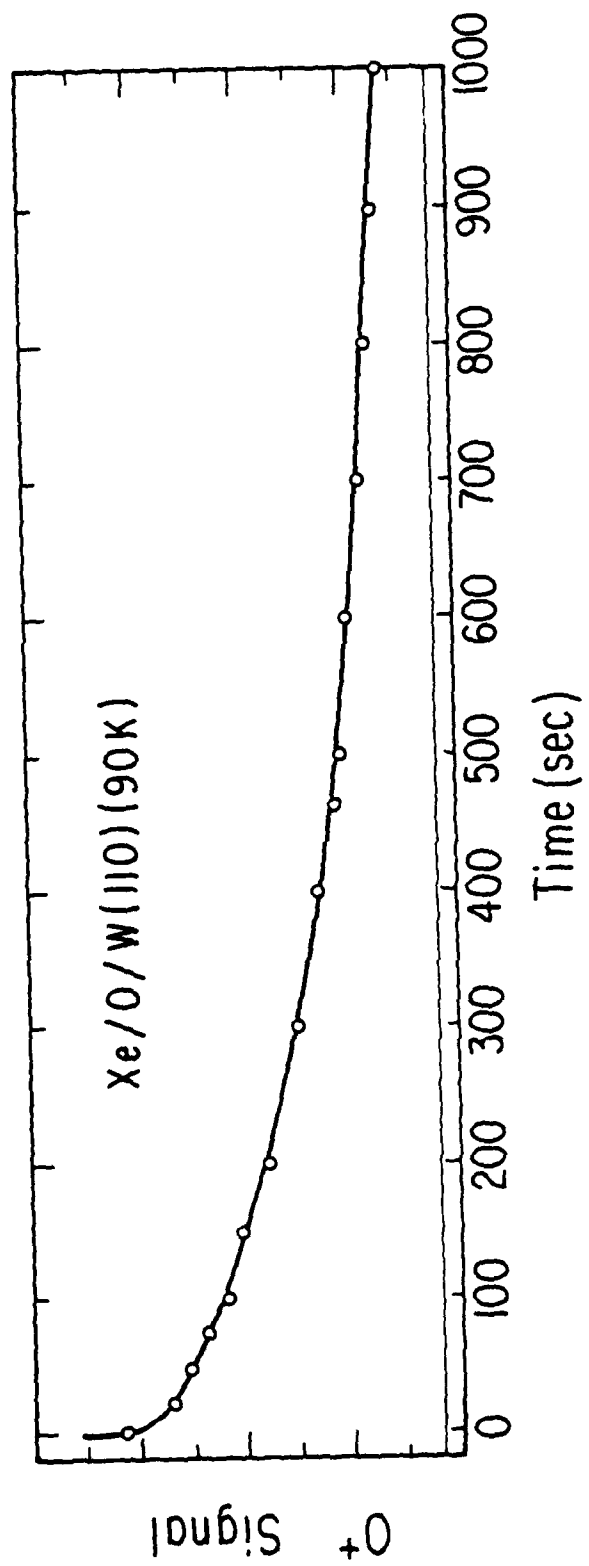
Time (sec)

Xe Mass Spectrometer Signal

Fig. 4

Xe/W(110)
Fast Decay

Fig. 2

Fig. 3

Xe/O/W(110)(90K)

O⁺ Signal

Time (sec)

Fig.4

Xe/O/W(110)(90K)

Xe Signal

Time (sec)

Fig. 5